Short communication

Mg–Al layered double hydroxides containing glycine betaine as low humidity-dependent anion conducting electrolyte material for Solid State Alkaline Fuel Cell (SAFC)

Peilin Zhang [a], Sumihito Sago [a], Takeo Yamaguchi [b], Gopinathan M. Anilkumar [a],*

[a] Research & Development Center, Noritake, Co., Ltd., 300 Higashiyama, Miyoshi cho, Miyoshi, Aichi 470-0293, Japan
[b] Chemical Resources Laboratory, Tokyo Institute of Technology, R1-17, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

HIGHLIGHTS

► High anionic conductivity at low humidity by intercalating betaine into layered double hydroxide.
► Higher durability under long time evaluation than unmodified LDH.
► Novel organic-inorganic hybrid LDHs as anion conducting materials for solid alkaline fuel cells.

GRAPHICAL ABSTRACT
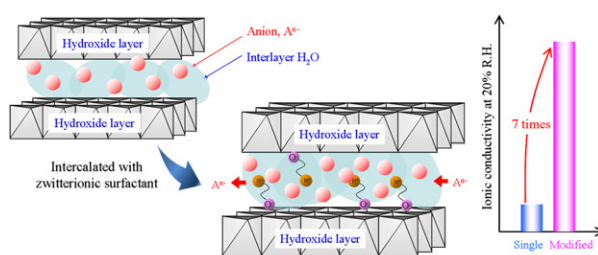
ARTICLE INFO

ABSTRACT

The ionic conductivity of organically modified Mg–Al layered double hydroxide (LDH) with respect to various humidity conditions was investigated. Glycine betaine (zwitterionic surfactant) $[(CH_3)_3N^+CH_2COO^-]$ intercalated LDHs were prepared by a co-precipitation method, and were characterized by XRD, TG-DTA, and FTIR techniques. The samples were pressed into pellets and their ionic conductivities were evaluated by complex impedance method. The results revealed that the intercalation of glycine betaine weakened the interaction between interlayer anion with H_2O molecules, and favored to form more free H_2O molecules inside the interlayer. The ionic conductivity value (80 °C) of LDH was significantly enhanced from 5.6×10^{-5} S cm^{-1} to 3.9×10^{-4} S cm^{-1} at 20% R.H by the intercalation of zwitterionic surfactant. The betaine intercalated LDH also showed much higher stability in all the humidity ranges and showed a conductivity value of 5.1×10^{-3} S cm^{-1} at 80% RH, even after 200 h of operation.

1. Introduction

The first successful application of fuel cells can be traced back to the middle of last century, where fuel cells (Alkaline Fuel Cells, AFCs) were loaded in NASA Apollo spacecraft for power and water supply. Comparing with other fuel cells, AFCs offer some great advantages including mild operating temperature, high energy density, and also avoiding precious noble catalyst materials such as platinum in the catalyst layer. However, AFCs didn't become popular, mainly due to the use of liquid electrolyte (eg: KOH solution) which is unstable to CO_2 in atmosphere. To solve this problem, solid anion exchange membranes are being developed by various research groups [1,2], which usually involve polymeric materials. However, chemical/thermal stability seems to be a huge challenge for pure organic membranes. Designing organic—inorganic hybrid electrolytes could be an option to overcome the stability issues,

* Corresponding author. Tel.: +81 561 34 6215; fax: +81 561 34 4997.
E-mail address: ganilkumar@n.noritake.co.jp (G.M. Anilkumar).

without compromising the anion conducting property. For PEMFC (proton exchange membrane fuel cell) systems, to enhance the ionic (proton) conductivity and chemical/thermal stability of polymeric membranes, incorporation of suitable proton conducting inorganic nanoparticles have been widely reported [3–9]. Similarly, suitable inorganic anion conducting materials are required for fabricating composite membranes for AFC systems.

The most well known and naturally occurring anionic clays (inorganic) are the hydrotalcite type layered double hydroxides (LDHs), which are composed of positively charged hydroxides layers with negatively charged ions (anions) and H_2O molecules in the interlayer [10]. Because of their unique structure and properties, these materials find various applications in the fields of anion exchangers, catalysts, electrochemical sensors etc. Recently, LDHs as potential candidate for alkaline fuel cell application have been investigated and the anion conductivities of Mg–Al LDHs at high humidity condition were reported [11–13]. Furthermore, the application of LDH as hydroxide ion conductive electrolyte material in alkaline fuel cells [14] and alkaline-type direct ethanol fuel cells [12] were also reported. However, it was also reported that low humidity would cause a drastic decrease in the anionic conductivity of Mg–Al LDHs [11].

Poor ionic conductivity under low humidity is always a challenging problem for various electrolytes, which means an external humidifier is necessary to ensure the fuel cell working at the required humidity. This would not only make the system complicated and increase the cost, but also cause slow response on startup. Therefore, the development of low humidity-dependent anion conducting materials is very important for the commercialization of AFCs. The ionic conductivity of LDH is closely related to the interlayer structure; especially the anions and water molecules in the interlayer. The influence of interlayer inorganic anions has already been investigated [11], and in this research, we focus on the modification of LDH with organic surfactants. Considering the block effect of long chain organics, and the compromising of positive charged site in interlayer by anionic surfactant, which would cause decrease in ionic conductivity, a short chain zwitterionic surfactant, glycine betaine, was selected to modify LDH. Glycine betaine is a typical zwitterion, which can be intercalated into the interlayer of LDH [15]. Further, the presence of the tetra-alkylammonium head groups, $\{(CH_3)_3N^+R\}$, in the zwitterion is also expected to increase the anion conduction. Therefore, in this paper we report the introduction of glycine betaine $[(CH_3)_3N^+CH_2COO^-]$ into an inorganic material, Mg–Al LDH, to enhance its ionic conductivity at low humidity. To the best of our knowledge, this is the first report on the fabrication of low-humidity high ionic conducting material.

2. Experimental

2.1. Synthesis

The Mg–Al LDH was prepared by a co-precipitation method, using magnesium and aluminum nitrates as starting materials [16]. In a typical synthesis, a mixed solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was first prepared with $Mg^{2+}/Al^{3+} = 3$, followed by the addition of Na_2CO_3 solution. The solution was vigorously stirred for 20 min, and then, the pH of the mixed solution was adjusted to 9.5 by dropwise addition of 4M NaOH solution. After 30 min of stirring, the solution was kept at 80 °C for 4 h. The precipitate was recovered by centrifugation and washed with distilled water, and finally dried at 80 °C, overnight.

To prepare glycine betaine zwitterion $[(CH_3)_3N^+CH_2COO^-]$ intercalated LDH, the method followed was similar to that described above, except that instead of using Na_2CO_3 solution, glycine betaine solution was added and the reaction time was prolonged to 24 h. The

molar ratio of $Mg^{2+}:Al^{3+}:$glycine betaine was 3:1:2. The obtained sample was assigned as LDH + B.

2.2. Characterizations

The LDH and LDH + B samples were characterized by powder X-ray diffractometry (RINT-TTRIII, Rigaku, Japan) to identify the crystalline phases. FT-IR spectra were recorded on a Digilab FTS 7000 spectrometer. CHN analysis (Yanaco, CHN Corder, MT-6) was carried out to determine the nitrogen amount in the sample. The thermogravimetric analysis was performed on a thermal analyzer (Thermo plus TG-8120, Rigaku, Japan).

2.3. Conductivity measurement

The ionic conductivities of the samples were measured via AC impedance method using a Solartron Interface 1260 gain phase analyzer over the frequency range of $1–10^7$ Hz. For the measurement, sample pellets with a diameter of 10 mm and a thickness of 1.5 mm were prepared by the uniaxial pressing technique. Ag paste was smeared on both sides, followed by electroding it with Au wire. The samples were placed inside the temperature-humidity controlled oven (SH-221, ESPEC, Japan) and the measurements were carried out under the relative humidity of 80% at different temperatures (30–80 °C), and at 80 °C under various humidity conditions (20–80% R.H).

3. Results and discussion

By the CHN analysis, the carbon and nitrogen contents in the samples were measured. We assumed an ideal condition that no carbonate was incorporated in to LDH + B, since sodium carbonate was not used during the synthesis. Then, the anion contents were calculated and are presented in Table 1. The results suggested that besides carbonate ions, nitrate ions were also incorporated in LDH sample. The amount of incorporated glycine betaine was low under our experimental conditions.

The XRD patterns of the as made Mg–Al LDH samples are shown in Fig. 1. All the peaks observed on LDH (Fig. 1) correspond to the characteristic peaks of $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ (JCPDS 22-0700). The interlayer distance d_{003} calculated from Bragg's equation was 0.78 nm. The sharp diffraction peaks indicated good crystallinity especially along the z axis. Furthermore, the crystallite size was 18.2 nm calculated using Scherrer equation. The XRD pattern of betaine (zwitterionic surfactant) intercalated LDH (LDH + B) is also shown in Fig. 1. The intercalation of betaine was indicated by a small shift in the diffraction peaks to the small 2-theta angle direction, and the d value was calculated as 0.82 nm. In the past few years, many organic/polymer molecules were intercalated into LDHs for the potential application as drug supports/matrices [17], reactive adsorbents [18], catalysts [19], etc.. The interlayer distance (d) increases as the organic/polymer chain length increases [17–19]. Since the molecular size as well as the chain length of glycine betaine was small and the incorporated amount was low, only a slight increase in the d value was observed. However, the LDH + B sample showed broader peaks, compared to unmodified LDH, and

Table 1
Concentration of intercalated agents.

Sample	Anion content/mmol g^{-1}		
	Betaine	Nitrate	Carbonate
LDH	–	1.28	1.30
LDH + B	0.09	2.81	–

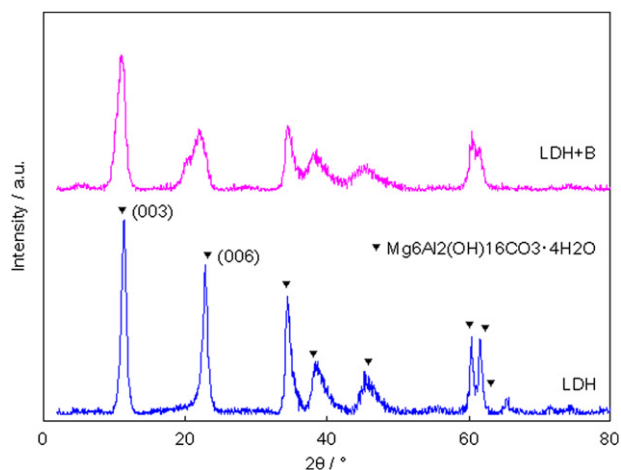Fig. 1. XRD patterns of the samples.

Fig. 3. FTIR spectra of the samples.

the crystallite size was calculated as 7.2 nm, which indicated that the incorporation of zwitterionic surfactant controlled the crystal growth.

TG-DTA analysis was carried out to investigate the thermal decomposition behaviors of the samples. $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ usually shows weight loss in two-stages, corresponding to the removal of water molecules (physisorbed, crystallization water and OH^- groups bonded to different cations) and the dehydroxylation of metal hydroxides together with the decomposition of inside anions [20]. Weight losses under 250 °C were usually due to the loss of adsorbed water and loosely held water in the interlayer space [21]. From the graph (Fig. 2), it is obvious that the initial weight loss of water in sample LDH + B completed below 200 °C, but for the sample LDH, large weight loss occurred between 200 °C and 250 °C. The results indicated that the thermal dehydration of LDH occurred at a higher temperature, in other words, water was strongly bonded in the interlayer. Contrarily, the water in LDH + B could be more easily eliminated, suggesting the loose bond between water molecules and hydroxide layers. The relatively larger d-spacing and presence of the quaternary ammonium group of the modified LDH have contributed to such a phenomenon.

Fig. 3 shows the FTIR spectra of LDH and LDH + B. Bands in the frequency range from 500 to 1100 cm^{-1} are due to various lattice vibrations associated with metal hydroxide sheets [22]. Strong band
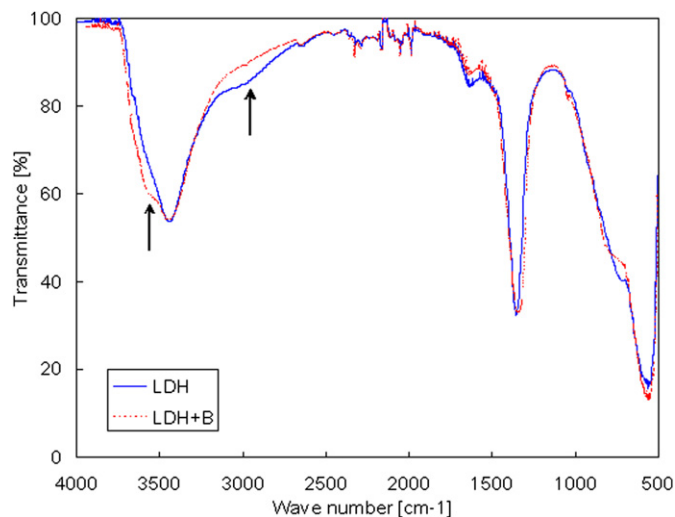
around 1350 cm^{-1} observed on both samples was attributed to the stretching mode of CO_3^{2-} or NO_3^- anions accommodating in the interlayer [21,23,24]. A shoulder peak present around 3000–3100 cm^{-1} observed on LDH's spectrum is caused by the interaction between the anion and H_2O present in the interlayer region [25,26]. However, the shoulder peak became weak on LDH + B, indicating that the intercalation of betaine weakened the interaction between anion and H_2O. Broad band in the range 3200–3700 cm^{-1} was observed in both samples, assigned to the O–H stretching vibration of the metal hydroxide layer and interlayer water molecules, which involves mostly hydrogen bonds [22]. Comparing the spectrum of LDH + B with that of LDH, an extra band around 3600 cm^{-1} emerged, indicating the different bonding structure of H_2O in the LDH + B. It was reported that shift toward high frequency of bending mode usually related to the interaction between loose bonds [27]. Hence, it is proposed that the proportion of loosely bonded or even free H_2O in the interlayer became large after intercalated with betaine. These results agree well with that obtained by TG-DTA analysis as discussed above. The amount and the distribution of H_2O play an important role in the ionic
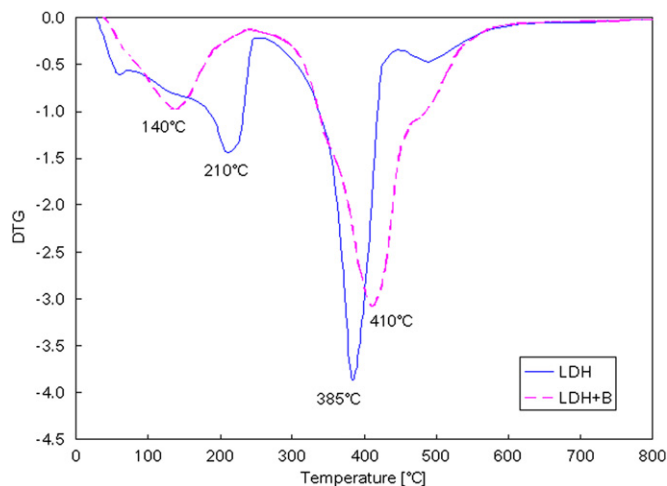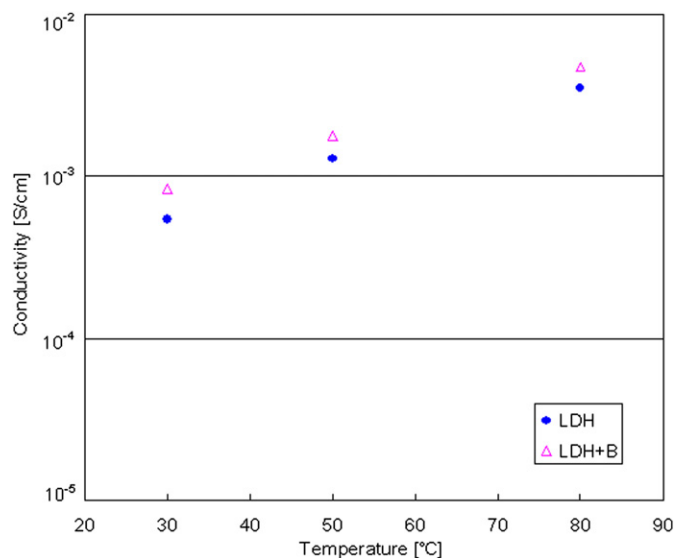

Fig. 2. DTG spectra of the samples.

Fig. 4. Ionic conductivities of the samples at different temperatures (80%R.H).
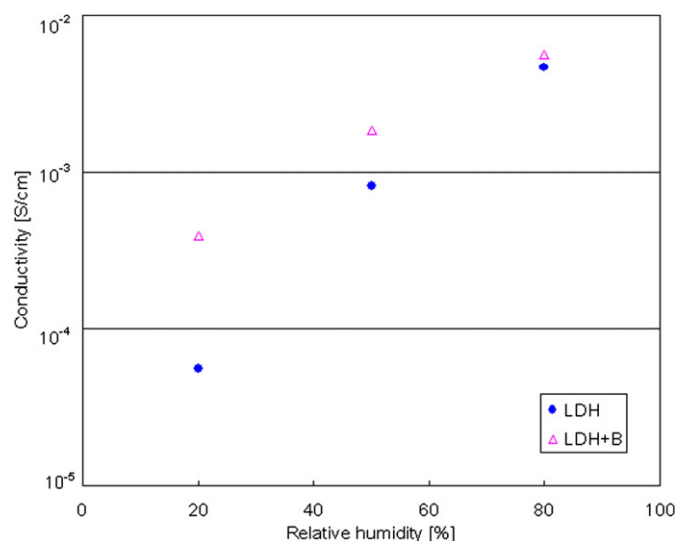
Fig. 5. Ion conductivities of the samples measured at 80 °C under different humidity.

conductivity of LDH. It is reasonable to expect that LDH + B could show a different ion conducting behavior compared to that of unmodified LDH. However, more detailed investigations are required to understand the conduction mechanisms.

The ionic conductivity of the samples was evaluated by complex impedance method.

The temperature dependency of ionic conductivity of sample at 80% R.H. is presented in Fig. 4. As the temperature increased from 30 °C to 80 °C, the ionic conductivity also increased, further in all the measured temperatures the hybrid LDH showed higher ionic conductivity compared to its counterpart.

Through the test with the concentration cell using sodium hydroxide solution, and further investigation of electromotive force (EMF), it was proved that the ionic conductivity of LDH is due to the interlayer anions [12]. There are three kinds of possible anions accommodating in the interlayer of LDH, CO_3^{2-}, NO_3^-, and OH^-. From the CHN analysis (Table 1), we clearly identified that both

CO_3^{2-} and NO_3^- ions exist in the single LDH, and are the main charge carriers. In the case of LDH + B, considering the fact that no sodium carbonate was used during the synthesis of LDH + B, we believe that the main charge carrier ion should be NO_3^-. The influence of intercalated anions on the ionic conductivity of Mg—Al LDH has been investigated, and demonstrated that Mg—Al LDHs intercalated with CO_3^{2-}, NO^-, or Cl^-, all showed very similar ionic conductivity [11].

The anion conductivity data (80% R.H.) of LDH and LDH + B at different temperatures is presented in Fig. 4. It is clear from the data that the LDH + B samples have higher ionic conductivity than that of LDH in all the measured temperature. The enhanced anionic conductivity of LDH + B can be attributed to the intercalation of glycine betaine, which can weaken the bond between water molecules and interlayer to provide more free water as discussed from the TG-DTA and FTIR results, but also introduce tetra-alkylammonium head groups $\{(CH_3)_3N^+R\}$ (a well known OH-conductor—widely used in polymeric anion conducting membrane) into LDH.

Fig. 5 shows the ionic conductivities of the samples evaluated at 80 °C under different relative humidities. The prepared LDH showed a high ionic conductivity of 4.6×10^{-3} S cm^{-1} at a relative humidity of 80%, and it decreased to 5.6×10^{-5} S cm^{-1} at a low relative humidity of 20%. This behavior is similar to that of most ion conducting electrolytes which usually show high ionic conductivity under high humidity, and very low conductivity under low humidity. This tendency should have a close relationship with H_2O molecules in the samples, since they are considered to form channels which control the mobility of ions. Similar results were also reported by other group [11], and the reason for the decrease in ionic conductivity was attributed to the dehydration of the Mg—Al LDH in dry environment. Comparing with LDH, the ionic conductivity of LDH + B also decreased when the relative humidity decreased from 80 to 20 %, however, the ionic conductivity of LDH + B at 20% R.H. was almost 7 times higher than that of LDH (LDH: 5.6×10^{-5} S cm^{-1}; LDH + B: 3.9×10^{-4} S cm^{-1}). In other words, the decrease in ionic conductivity of LDH at low humidity was significantly mitigated by the intercalation of glycine betaine. The above characterization revealed that more loosely bonded or even free H_2O molecules existed in the interlayer of
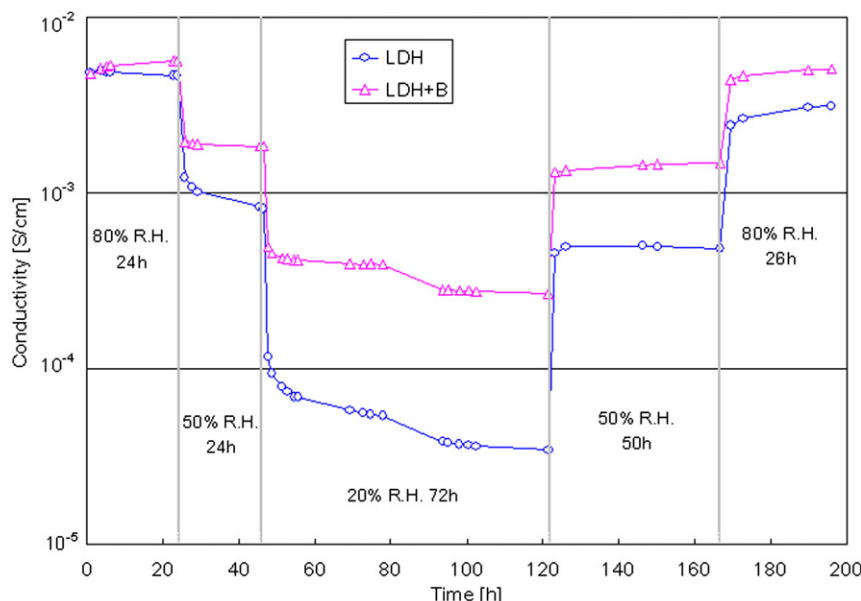

Fig. 6. Durability measurement results of single LDH and LDH + B.

LDH + B, and which probably favored the formation of ion conducting channels more easily even under low humidity environment. Furthermore, the structure of the zwitterionic surfactant, glycine betaine $\{(CH_3)_3N^+CH_2COO^-\}$, used in this study, could also be an important factor to enhance the ionic conductivity. In the case of zwitterionic surfactant, although the acetic groups would occupy the cationic sites of LDH, tetra-alkylammonium head groups $\{(CH_3)_3N^+R\}$ could absorb inorganic anions to guarantee adequate amount of anions for ion conducting. At the same time, the introduction of $\{(CH_3)_3N^+R\}$ into LDH could also favor the ion conducting through a Grotthuss mechanism which is reported for polymer based anion exchange membranes [28]. The prepared organically modified LDH particles are also expected to show high compatibility with polymer electrolyte in terms of anion conductivity, stability and durability in the design of anion conducting hybrid membranes.

The durability of the prepared LDH samples was also evaluated, and the results are shown in Fig. 6. The sample pellets were kept at 80 °C under 80% R.H., and lowered to 50% R.H. and to 20% R.H. for different intervals of time (>24 h), then, the humidity was again raised from 20% to 80% R.H. and the ionic conductivities were measured. The results revealed that after one cycle of measurement (200 h), the ionic conductivity of single LDH at 80% R.H. decreased from 4.6×10^{-3} S cm^{-1} to 3.1×10^{-3} S cm^{-1}, with a decreasing ratio of 32.6%. However, the LDH + B maintained high ionic conductivity and the decreasing ratio was as low as 8.9%. Furthermore, after keeping at 20% R.H. for 72 h., there is a drastic decrease in ionic conductivity of unmodified LDH compared to that of the hybrid LDH. This clearly indicates that the stability and durability of betaine intercalated LDH are quite high under all humidity conditions.

4. Conclusions

A high ion conducting material under low humidity was successfully fabricated by the intercalation of glycine betaine into MgAl-LDH. The intercalated glycine betaine could weaken the interaction between CO_3^{2-} and H_2O molecules, and increase the proportion of loosely bonded H_2O, which is estimated to be effective to enhance the ionic conductivity of LDH at low humidity condition (R.H. 20%). Furthermore, the hybrid LDH material also showed high stability and durability under various humidity conditions compared to that of the normal Mg-Al LDH. The application of LDH as a hydroxide ion conductive electrolyte material for alkaline fuel cell has recently been reported and is receiving increasing interest. Hence, this organically modified LDH is expected to find potential application in the development of composite hybrid electrolyte membranes for alkaline fuel cells.

References

[1] H. Jung, K. Fuji, T. Tamaki, H. Ohashi, T. Ito, T. Yamaguchi, J. Membr. Sci. 373 (2011) 107–111.
[2] E.S. Switzer, T.S. Olson, A.K. Datye, P. Atanassov, M.R. Hibbs, C. Fujimoto, C.J. Cornelius, Electrochim. Acta 55 (2010) 3404–3408.
[3] J.M. Lee, H. Ohashi, T. Ito, T. Yamaguchi, J. Chem. Eng. Jpn. 42 (2009) 918–929.
[4] K.T. Park, U.H. Jung, D.W. Choi, K. Chun, H.M. Lee, S.H. Kim, J. Power Sourc. 177 (2008) 247–253.
[5] G.M. Anilkumar, S. Nakagawa, T. Okubo, T. Yamaguchi, Electrochem. Comm. 8 (2006) 133–136.
[6] R. Jiang, H.R. Kunz, J.M. Fenton, Electrochim. Acta 51 (2006) 5596–5605.
[7] A. Sacća, I. Gatto, A. Carbone, R. Pedicini, E. Passalacqua, J. Power Sourc. 163 (2006) 47.
[8] N.H. Jalani, K. Dunn, R. Datta, Electrochim. Acta 51 (2005) 553.
[9] M. Watanabe, H. Uchida, M. Emori, J. Phys. Chem. B 102 (1998) 3129.
[10] V. Rives, Layered Double Hydroxides: Present and Future, Nova Science Publishers, Inc., New York, 2001, pp. 1–8.
[11] Y. Furukawa, K. Tadanaga, A. Hayashi, M. Tatsumisago, Solid State Ionics 192 (2011) 185–187.
[12] K. Tadanaga, Y. Furukawa, A. Hayashi, M. Tatsumisago, Adv. Mater. 22 (2010) 4401–4404.
[13] H.S. Kim, Y. Yamazaki, J.D. Kim, T. Kudo, I. Honma, Solid State Ionics 181 (2010) 883–888.
[14] D. Kubo, K. Tadanaga, A. Hayashi, M. Tatsumisago, J. Power Sourc. 222 (2013) 493–497.
[15] T. Hibino, W. Jones, J. Mater. Chem. 11 (2001) 1321–1323.
[16] Walter T. Reichle, Solid State Ionics 22 (1986) 135–141.
[17] G.J. Hu, H.X. Wang, L.Y. Liu, M. Pu, J. He, D.G. Evans, J. Phys. Chem. Solids 71 (2010) 1290–1294.
[18] K.B. Ayala-Luis, C.B. Koch, H.C. Hansen, Appl. Clay Sci. 48 (2010) 334–341.
[19] F. Kovanda, E. Jindova, K. Lang, P. Kubat, Z. Sedlakova, Appl. Clay Sci. 48 (2010) 260–270.
[20] J.S. Valente, G. Rodriguez-Gattorno, M. Valle-Orta, E. Torres-Garcia, Mater. Chem. Phys. 133 (2012) 621–629.
[21] Q. Wang, Z. Wu, H.H. Tay, L. Chen, Y. Liu, J. Chang, Z. Zhong, J. Luo, A. Borgna, Catal. Today 164 (2011) 198–203.
[22] W. Kagunya, R. Baddour-Hadjean, F. Kooli, W. Jones, Chem. Phys. 236 (1998) 225.
[23] J.T. Kloprogge, R.L. Frost, J. Solid State Chem. 146 (1999) 506.
[24] F.M. Labajos, V. Rives, M.A. Ulibarri, J. Mater. Sci. 27 (1992) 1546.
[25] J.T. Kloprogge, R.L. Frost, Appl. Catal. A 184 (1999) 61.
[26] J.T. Kloprogge, R.L. Frost, Phys. Chem. Chem. Phys. 1 (1999) 1641.
[27] V. Rives, Layered Double Hydroxides: Present and Future, Nova Science Publishers, Inc., 2001, p. 203.
[28] G. Merle, M. Wessling, K. Nijmeijer, J. Membr. Sci. 377 (2011) 1–35.